Syntheses of Some Lanthanoid Complexes with 4,7,13,16,21,24-hexaoxa-1, 10-diazabicyclo[8.8.8]hexacosane. Crystal Structure of a Europium(III) Perchlorate Derivative

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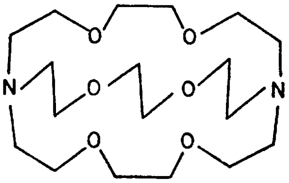
Summary The crystal structure of $[Eu(ClO_4)<222>](ClO_4)_2.MeCN$ ($<222>$ = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) shows that the europium(III) ion is ten-co-ordinate to the eight donor atoms of the cryptand and to two oxygen atoms of a ClO_4^- ion; the geometry of the co-ordination polyhedron can be described in terms of a bicapped square antiprism.

THE co-ordination compounds of several diaza-polyoxa-macrobicyclic ligands with alkali and alkaline earth ions or actinoid and transition metal ions have been extensively studied.[1] A preliminary report on the synthesis and solution behaviour of some lanthanoid cryptates has recently appeared.[2] The crystal structure of the compound $[La(NO_3)_2<222>]_3[La(NO_3)_6].2MeOH$ ($<222>$ =4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) has also recently been reported.[3]



⟨222⟩

The reaction of anhydrous lanthanoid perchlorates with the cryptand <222> in MeCN gives compounds of formula $Ln(ClO_4)_3$.<222>.MeCN (Ln = Pr, Nd, or Eu). Traces of water caused the separation of complexes of formula $Ln(ClO_4)_3$.<222>.H_2O.0·5MeCN (Ln = La, Ce, Sm, Eu, Dy, or Ho). The structure of the anhydrous europium derivative has been determined by *X*-ray analysis.

Crystal data: $C_{20}H_{39}Cl_3EuN_3O_{18}$, $M = 867{\cdot}88$, orthorhombic, space group $P2_12_12_1$, $a = 33{\cdot}567$, $b = 10{\cdot}646$, $c = 8{\cdot}821$ Å, $U = 3152{\cdot}2$ Å^3, $Z = 4$, $F(000) = 1752$, μ(Mo-K_α) = 23·2 cm^{-1}, D_c = 1·84 g cm^{-3}. Intensity data (1037 unique observed reflections in the range $3 < \theta < 20°$) were collected on a PW 1100 Philips diffractometer with monochromatic Mo-K_α radiation. Absorption corrections were applied. The structure was solved using the heavy atom technique and successive F_0 Fourier syntheses. The absolute structure, obtained by introducing anomalous dispersion corrections for Eu and Cl atoms, was refined by full matrix least squares to a conventional *R* factor of 0·072.†

The structure consists of [Eu(ClO_4)<222>]$^{2+}$ cations, of ClO_4^- anions, and of interposed MeCN solvent molecules. The europium(III) ion is ten-co-ordinate, linked to the eight donor atoms of the cryptand and to two oxygen atoms of a perchlorate ion (Figure). The geometry of the co-ordination polyhedron can be described in terms of a bicapped square antiprism with the two nitrogen atoms at the apices [$\angle$ N–Eu–N = 179·4(1·4)°]. The Eu–N distances are 2·70(5) and 2·64(3) Å; the Eu–O(perchlorate) distances are 2·71(4) and 2·67(4) Å; the mean value of the Eu–O(ether) distances is 2·49 Å, ranging from 2·44(4) and 2·52(3) Å. These Eu–N and Eu–O(ether) bond distances compare well with the analogous distances found in nine- and ten-co-ordinate lanthanoid complexes [La–N(tertiary amine) = 2·86[4] and 2·75[5] Å; Nd–O(ether) = 2·52[6] Å]. Shortening of all these distances in the present complex reflects the smaller ionic radius of europium(III).[7]

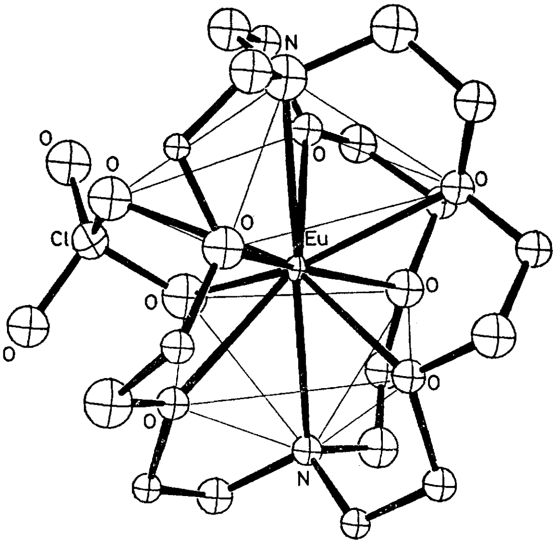


FIGURE. ORTEP diagram of the [Eu(ClO_4)<222>]$^{2+}$ ion.

The samarium and europium complexes show very broad charge transfer bands with maxima at 41,300 and 32,100 cm^{-1}, respectively. A value of 3·0 can thus be assigned to the optical electronegativity of the cryptand <222>.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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